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EXAMINER	
LOUIE, MANDY C	

ART UNIT	PAPER NUMBER
1715	

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Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No.	Applicant(s)	
	10/584,642	MURAKAMI ET AL.	
	Examiner	Art Unit	
	MANDY C. LOUIE	1715	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *03 January 2011*.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1-8,11-16 and 18-24* is/are pending in the application.

4a) Of the above claim(s) *15,16 and 18* is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *1-8,11-14 and 19-24* is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *04/29/08, 06/13/07, 06/26/06*.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____.
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

DETAILED ACTION

Withdrawal on Election of Species Requirement

1. Examiner acknowledges the election of Group I, claim(s) 1-9, 11-14 and 19-24, in response filed on 09/30/10, and further upholds restriction is proper between all distinct inventions. However, due to applicant's amendments (amended claims 2, 6, and 19, and cancelled claim 9, filed on 01/03/11), the examiner withdraws election of species requirement (mailed on 12/03/10) since the amendments renders the election of species moot. Therefore, pending claims 1-8, 11-14, 19-24 will be examined. It is noted that any future amendment made into the method claims may cause a late restriction.

Claim Objections

1. Claim 1 is objected to because of the following informalities: "in supply limited region" is suggested to be changed to "in a supply limited region" and "in reaction limited region" is suggested to be changed to "in a reaction limited region". Appropriate correction is required.

2. Claim 19 is objected to because of the following informalities: "a first step…the chamber with a flow rate ratio…" is suggested to be changed to "a first step…the chamber with flow rate ratio…"; and "a second step…the chamber with the flow rate ratio of..." is suggested to be changed to "a second step…the chamber with flow rate ratio of…". Appropriate correction is required.

Specification

3. The disclosure is objected to because of the following informalities: since claims 6 and 19 were amended to better reflect the disclosure from paragraphs 0052-0056 in the applicant's specification (and also to be more consistent with dependent claims 7-8, 20-23), it is request that the term "flow rate ratio of the titanium tetrachloride to the ammonia" in paragraph 0009 of the specification be changed to "flow rate ratio of the ammonia to the titanium tetrachloride" to be more consistent with the present amendments.

Appropriate correction is required.

Claim Rejections - 35 USC § 112

1. The following is a quotation of the second paragraph of 35 U.S.C. 112:

> The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

2. Claim 20 is rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

a. As to claim 20, which can depend upon claim 19, the limitation of "flow rate ratio in the first step is not more than 60, and...flow rate ratio in the second step is not more than 16" is indefinite since such limitation is broader than of claim 19, which already recites a more narrow flow rate ratio ranges for the first step and second step (i.e. first flow ratio is not less than 2.5 but more than 60, and the second flow rate ratio is not less than 0.3 but not more than 10).

Claim Rejections - 35 USC § 102

1. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

4. Claims 1-2 are rejected under 35 U.S.C. 102(b) as being anticipated by Fiordalice [Us 5420072].

As to claim 1, Fiordalice teaches a method for forming titanium nitride film on a substrate [title] by reacting titanium tetrachloride and ammonia [col 2, ln 65-67], the method comprising a first step of reacting titanium tetrachloride and ammonia with each other; thereby forming a first titanium nitride layer on the substrate [col 2, ln 61-68], where the supply of reaction gases is limited by a range of partial pressures that reacts within a predetermined chamber volume (supply limited region) [col 3, ln 19-26]; and a second step of reacting titanium tetrachloride and ammonia with each other; thereby forming a second titanium nitride layer on the first titanium nitride layer [col 3, ln 48-54]. Although the prior art does not explicitly teach the second step occurring in a reaction limited region, it would have been inherent to the prior art that the specified partial pressure ranges for the reaction gases and predetermined chamber volume of the second step would induce reaction at the substrate surface in a reaction limited manner (since the prior art teaches the second step requires a higher TiCl4 to NH3 partial pressure ratio [col 3, ln 20-22], the reaction of the second step is limited by how much

TiCl4 can react with NH4 to form the second film, due to the higher TiCl4 partial pressure; therefore, the second step is reaction-limited by the potential chemical reactions that can occur between the two gases at the substrate).

As to claim 2, Fiordalice exemplifies the partial pressure ratio of TiCl4/NH3 in the first step is lower (0.05mTorr of TiCl4, 30mTorr of NH3; ratio of 0.00167) [col 3, ln 20-22] than of the ratio in the second step (11mTorr of TiCl4, 30mTorr of NH3; ratio of 0.367) [col 4, ln 11-13].

Claim Rejections - 35 USC § 103

1. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

2. The factual inquiries set forth in *Graham* **v.** *John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

3. This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein

were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

5. Claim 3 is rejected under 35 U.S.C. 103(a) as being unpatentable over Fiordalice.

Teaching of Fiordalice is aforementioned.

As to claim 3, Fiordalice teaches the range of the partial pressure ratio in the first step can be 0.0001-0.1 (TiCl4 partial pressure range/ NH4 partial pressure range) [col 3, ln 4-6] and the second step can be 0.003-10 [col 4, ln 1-2], where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists. (See MPEP 2144.05.I). Although prior art does not explicitly teach the claimed range for the partial pressure ratio in the first step, it would have been obvious to one of ordinary skill in the art to optimize the partial pressure ratio of the first step via routine experimentation, since Fiordalice teaches these parameters affect film properties of TiN (i.e. crystal orientation, col 3, ln 8-12).

4. Claims 1-5 are rejected under 35 U.S.C. 103(a) as being unpatentable over Fiordalice in view of Miyamoto [US 5840628].

Teaching of Fiordalice is aforementioned, but in the case of Fiordalice failing to perform the first step in a supply limited region, and the second step in a reaction limited region. Miyamoto is provided.

As to claim 1, Miyamoto teaches a method of depositing TiN layers [abstract] where the first step is provided in a process which the Ti-based gas is made low (supply limited) to yield a high purity TiN layer [col 4, ln 7-14] and the second step the Ti-based gas is made high so as to provide the gas sufficiently; therefore the surface reaction occurs at a limited rate (reaction limited), so as to improve step coverage [col 4, ln 15-20].

It would have been obvious to one of ordinary skill in the art at the time of the invention to provide the first step in a supplied limited region, and the second step in a reaction limited region at the time of the invention, so as to form the first TiN layer with lower impurities and the second TiN layer with better step coverage [col 4, ln 12-14; 20].

As to claim 2, Fiordalice exemplifies the partial pressure ratio of TiCl4/NH3 in the first step is lower (0.05mTorr of TiCl4, 30mTorr of NH3; ratio of 0.00167) [col 3, ln 20-22] than of the ratio in the second step (11mTorr of TiCl4, 30mTorr of NH3; ratio of 0.367) [col 4, ln 11-13].

As to claim 3, Fiordalice teaches the range of the partial pressure ratio in the first step can be 0.0001-0.1 (TiCl4 partial pressure range/ NH4 partial pressure range) [col 3, ln 4-6] and the second step can be 0.003-10 [col 4, ln 1-2], where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists. (See MPEP 2144.05.I). Although prior art does not explicitly teach the claimed range for the partial pressure ratio in the first step, it would have been obvious to one of ordinary skill in the art to optimize the partial pressure ratio of the first

step via routine experimentation, since Fiordalice teaches these parameters affect film properties of TiN (i.e. crystal orientation, col 3, ln 8-12).

Teaching of Fiordalice is aforementioned, but appears to be silent in teaching the temperature of the substrate in the first step is lower than the second step (claim 4) or that the temperatures fall in the claimed ranges recited in claim 5. Miyamoto remedies this.

As to claim 4, Miyamoto teaches the surface temperature of the substrate is preferably higher in the second step than in the first step [col 6, ln 50-54], which would further contribute to the reduction of chlorine (impurities) content [col 6, ln 54-56].

It would have been obvious to one of ordinary skill in the art at the time of the invention to optimize the temperature range of Fiordalice (300-800 degrees Celsius, col 3, ln 3, 67) so that the substrate temperature is higher in the second step than the first step as suggested by Miyamoto. One would have been motivated to do so to reduce chlorine (impurities) content [Miyamoto, col 6, ln 54-56].

As to claim 5, although Miyamoto does not explicitly teach the claimed temperature ranges for the first step and second step, it would have been obvious to one of ordinary skill in the art to optimize the surface temperature to these ranges via routine experimentation, since Miyamoto teaches such modification reduces chlorine content in the TiN layer [col 6, ln 54-56].

6. Claims 6-7, 19-20, 23-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Wang [US 20020064598].

As to claim 6, Wang teaches a method of forming a TiN composite layer on a substrate [abstract] to be processed in a chamber [0024] through the reaction of titanium tetrachloride and ammonia [abstract], the method comprising: a first step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the ammonia to the titanium tetrachloride (NH3/TiCl4 flow rate ratio) being a first rate ratio [0010] at a chamber pressure range greater than 5 Torr (greater than 666.6Pa) [0033] thereby forming a first titanium nitirde layer on the substrate [0010], a second step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the ammonia to the titanium tetrachloride (NH3/TiCl4 flow rate ratio) being a second flow rate smaller than the first flow rate [0010], while the chamber pressure is held at a range greater than 5 Torr (greater than 666.6Pa) [0037]. Although Wang does not explicitly teach the claimed chamber pressure range, in the case where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists. (See MPEP 2144.05.I).

As to claim 7, Wang teaches the first flow ratio can be 40-250, and the second flow ratio can be 2.5-17, or 8.5 [0010]; where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists (See MPEP 2144.05.I).

As to claim 19, Wang teaches a method of forming a TiN composite layer on a substrate [abstract] to be processed in a chamber [0024] through the reaction of titanium tetrachloride and ammonia [abstract], the method comprising: a first step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the

ammonia to the titanium tetrachloride (NH3/TiCl4 flow rate ratio) being a first rate ratio [0010] thereby forming a first titanium nitirde layer on the substrate [0010], a second step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the ammonia to the titanium tetrachloride (NH3/TiCl4 flow rate ratio) being a second flow rate smaller than the first flow rate [0010], where the first flow rate ratio is from 40-250 and the second flow ratio is between 2.5-17, or about 8.5 [0010]; where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists (See MPEP 2144.05.I).

As to claim 20, Wang teaches the first flow rate ratio is from 40-250 and the second flow ratio is between 2.5-17, or about 8.5 [0010]; where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists (See MPEP 2144.05.I).

As to claim 23, Wang teaches the chamber pressure is held at a range greater than 5 Torr (greater than 666.6Pa) for first and second steps [0033, 0037]. Although Wang does not explicitly teach the claimed chamber pressure range, in the case where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists. (See MPEP 2144.05.I).

As to claim 24, Wang teaches the temperature of the substrate is in the range of 400-600 degrees Celsius [Table 1].

5. Claims 11-12 are rejected under 35 U.S.C. 103(a) as being unpatentable over Wang in view of Yamamoto [US 20020006739].

Teaching of Wang is aforementioned and teaches the first and second titanium nitride layers are formed while the substrate is placed in the chamber in the first and second step [0025, 0030-0031], but appears to be silent in teaching the method further comprising a step of purging an interior of the chamber with a purge gas after at least one of the first and second steps. Yamamoto remedies this.

As to claim 11, Yamamoto teaches a method for forming TiN film onto a surface [abstract], wherein after forming the TiN film, a step of purging gas with an inert gas is provided [0020].

It would have been obvious to one of ordinary skill in the art at the time of the invention to provide a purging step at either after the first step or second step of forming the TiN layers. One would have been motivated to do so to so as to purge the film forming chamber of the gas mixture or unreacted gas [0020] to remove any desired gases or components from the chamber.

As to claim 12, Yamamoto teaches argon is a known inert gas that is suitable for purging [0018]; and therefore it would have been obvious to have used argon as the purge gas because such gas would have been operable to successfully purge unwanted gases from the chamber with limited adverse effects.

6. Claims 8, 13-14 and 21 are rejected under 35 U.S.C. 103(a) as being unpatentable over Wang in view of Lee [US 20010002334].

Teaching of Wang is aforementioned, but appears to be silent in further teaching a step of annealing at least one of the first titanium nitride layer and the second titanium

nitride layer with a gas containing nitrogen atoms or hydrogen atoms after at least one of the first and second step. Lee remedies this.

As to claim 13-14, Lee teaches a method of forming a titanium nitride composite layer [title], where after a TiN layer is annealed with ammonia, the film is sufficiently densified and impermeable to Cl components [0046].

It would have been obvious to one of ordinary skill in the art at the time of the invention to provide a step of anneal with ammonia after forming a TiN layer in either the first step or second step. One would have been motivated to do so to densify the TiN layer and reduce Cl impurities within the layer [0046; 0066].

As to claims 8 and 21, Wang is aforementioned, but appears to be silent in teaching the first step is in a range of 2.5-15. Lee remedies this.

As to claims 8 and 21, Lee teaches the first TiN layer can have a firs gas flow ratio of TiCl4 to NH3 from 0.02-0.1 (NH3/TiCl4: 10-50) [0064]. In the case where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists. (See MPEP 2144.05.I).

It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the first gas flow ratio to the range taught by Lee. One would have been motivated to do so to lower the Cl component to yield a denser film [Lee, 0064] so deterioration rate of the semiconductor device is lower [Lee, 0032].

7. Claim 22 is rejected under 35 U.S.C. 103(a) as being unpatentable over Wang in view of Chen [US 20040198045].

Teaching of Wang is aforementioned, but appears to be silent in teaching the TiCl4 flow rate of the second step is from 9-130 sccm. Chen remedies this.

As to claim 22, Chen teaches a method of forming a titanium nitride layer [abstract], where a second deposition step for forming a TiN layer comprises a flow ratio of NH3/TiCl4 that is more than 5, and has a higher flowrate TiCl4 for faster deposition such as at least 25 sccm [0023].

It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the TiCl4 flow rate of the second deposited TiN layer of Wang as suggested by Chen. One would have been motivated to do so since Chen teaches a higher flowrate of TiCL4 would yield faster deposition (thus improving throughput), while yielding an operable TiN film that overlaps with the claimed flow ratio (NH3/TiCl4: greater than 5, 0023).

Conclusion

1. No claim is allowed.
2. All the pending claims are subject to restriction/election requirement.
3. Claims 15-15, 18 are withdrawn from restriction election.
4. Claims 1 and 19 are objected for the reasons aforementioned.
5. Claims 1-8, 11-14, 19-24 are rejected for the reasons aforementioned.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to MANDY C. LOUIE whose telephone number is

(571)270-5353. The examiner can normally be reached on Monday to Friday, 7:30AM - 5:00PM EST.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Timothy Meeks can be reached on (571)272-1423. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/M. C. L./
Examiner, Art Unit 1715

/Timothy H Meeks/
Supervisory Patent Examiner, Art Unit 1715